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The Adsorption of Isobutyramide at the Mercury/Aqueous Sodium Fluoride Solution Interface

by

W.R. Fawcett and A.J. Motheo

Prepared for Presentation

at

Electrochemical Society Meeting
Los Angeles, CA May 1989

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W.R. Fawcett, A.J. Motheo

The Adsorption of Isobutyramide at the Mercury/Aqueous Sodium Fluoride Solution Interface.

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We have recently been involved in a study of the adsorption of amides from aqueous solution at the mercury electrode [1]. The adsorptive behavior of these molecules is quite different from other organic systems, displaying characteristics which can be attributed to molecular reorientation. Some of these unusual interfacial properties can be attributed to the fact that these molecules have quite large dipole moments. The present study was concerned with the adsorption of isobutyramide (IBA) which can be classified as moderately strong compared to the adsorption of acetamide and dimethylacetamide [1].

The adsorption of IBA was studied by measuring the differential capacity of the mercury/solution interface as a function of electrode potential and adsorbate concentration, holding the concentration of the supporting electrolyte constant (0.25 m NaF). The reference electrode was a saturated calomel electrode (SCE), and the potential of zero charge was obtained using the streaming mercury electrode technique. The change in salt activity with IBA concentration was monitored with specific ion electrodes. These measurements also provided the factors to convert the SCE potential scale to one of thermodynamic significance. All experiments were conducted at 25°C.

Differential capacity against potential data for IBA concentrations in the range 0.01 to 1.0 M are shown in Fig. 1. These curves display a minimum at potentials negative of the *p.z.c.*, whose depth increases with IBA concentration. The maximum at more negative potentials is attributed to molecular desorption. The p.z.c. was observed to move in the positive direction with increase in IBA concentration, an observation which is attributed to adsorption of the molecular dipole with its positive end towards the metal in this potential region.

The capacity curves were twice integrated with respect to potential to obtain the relative surface tension. These data were then used to obtain the relative surface excess of IBA, Γ as a function of bulk activity for constant electrode charge density. The results, shown in Fig. 2, indicate that Γ reaches a maximum value at $\sim -4\ \mu C\ cm^{-2}$ for high bulk concentrations; however, at lower concentrations, Γ slowly increases as the electrode charge density is made more negative. Parry and Parsons [2] found similar behavior in adsorption of the p-toluene sulphonate anion at mercury and proposed a two-position isotherm to describe surface coverage. An analysis of the present data shows that reorientation of the IBA molecule occurs in the potential range in which adsorption is significant. The results of this analysis and the parameters of the adsorption isotherm are discussed in detail in this paper. The discussion also includes an analysis of the effects of ignoring variation in salt activity with increase in IBA concentration.

References

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2. J.M. Parry and R. Parsons, J. Electrochem. Soc., 113, 992 (1966).

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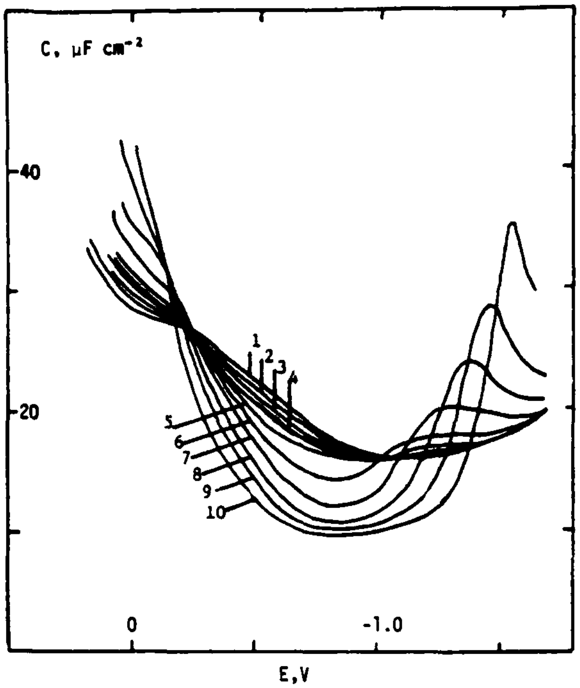

Fig. 1. Differential capacity against electrode potential for the Hg/solution interface for the system 0.25 m NaF + xm isobutyramide where x is equal to: 0(1), 0.01(2), 0.018(3), 0.032(4), 0.056(5), 0.10(6), 0.18(7), 0.32(8), 0.56(9) and 1.00(10).

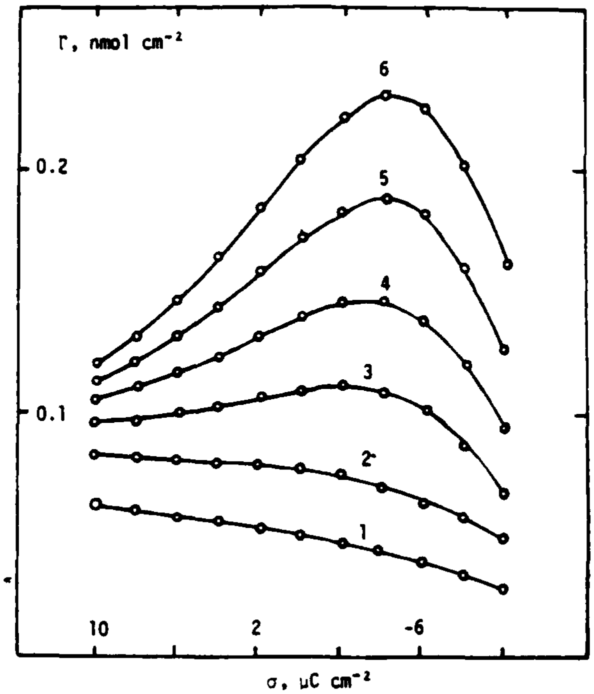

Fig. 2. Surface excess of isobutyramide against electrode charge density for various bulk concentrations: 0.01(1), 0.032(2), 0.10(3), 0.18(4), 0.32(5) and 0.56 m (6).